ELASTIC PROPERTIES OF MANGANESE ARSENIDE IN THE MAGNETIC TRANSFORMATION REGION

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Results of measurement of the temperature dependence of Young's modulus and the shear modulus, and also of the coefficient of thermal expansion, are presented for manganese arsenide in the temperature interval from room temperature to 460°K; this includes the magnetic transition temperatures of this compound (Θ_1 = 313°K and Θ_2 = 399°K). From the experimental data on the elastic moduli, the temperature variation of the compressibility of MnAs is calculated. At temperatures near Θ_2, large changes of Young's modulus and the shear modulus are observed, and also an abrupt change of the compressibility. In the vicinity of Θ_1, no anomalous changes in the elastic properties were detected. The results obtained are discussed in the light of two thermodynamic theories of magnetic phase transitions [5,6].

INTRODUCTION

THE nature of the magnetic transitions of manganese arsenide has not yet been explained. Experimental investigations of Guillaud[1] and Serres[2] have shown that at temperatures 313 and 399°K there occurs a change of the magnetic properties of MnAs. At low temperatures, manganese arsenide possesses ferromagnetic properties; at about 313°K, there occurs an abrupt decrease of magnetization, accompanied by a change of volume and the evolution of a latent heat of transition. In the temperature interval from 313 to 399°K, there occurs an increase of susceptibility with rise of temperature; and only above 399°K does MnAs become paramagnetic, with a temperature dependence of susceptibility that obeys the Curie-Weiss law. In Guillaud's opinion, such a change of magnetic properties can be explained by supposing that at Θ_1 = 313°K a transition occurs from the ferromagnetic to an antiferromagnetic state, and at Θ_2 = 399°K a transition from antiferromagnetism to paramagnetism.

This supposition has been supported by Meyer and Tagland[3], who investigated the magnetocaloric effect in MnAs and found changes of sign of the effect at temperatures 310 and 390°K. From thermodynamic considerations, it could be supposed that the observed increase of temperature on adiabatic demagnetization of a specimen is connected with an antiferromagnetic ordering of the spin magnetic moments of MnAs in the temperature interval in question. However, neutron-diffraction studies of Bacon and Street[4], and likewise antiferromagnetic-resonance studies, have failed to confirm the presence of antiferromagnetic ordering in this compound. This contradiction in the experimental data has led to diverse interpretations of the nature of the magnetic transitions in MnAs.

It was shown by Bean and Rodbell[5], that if, in the thermodynamic theory of magnetic transitions, account is taken of the dependence of the exchange-interaction integral on interatomic distances, then conditions can be realized under which the Curie-point transformation will be a phase transition of the first kind. It is natural that such effects should be observed in materials with a large compressibility and with a pronounced shift of the Curie temperature by pressure. Thus according to the view of Bean and Rodbell, the transformation in manganese arsenide at temperature 313°K is a transition from the ferromagnetic to the paramagnetic state, and the maximum of the susceptibility at 399°K is caused by the Jahn-Teller effect and is connected with structural changes of the lattice.

In the theory of Kittel[6], the magnetic transformation in manganese arsenide at 313°K is treated as a transition from the ferromagnetic to an antiferromagnetic state. The change in the type of magnetic order at the transition point is dependent on the fact that in this compound there are different types of exchange interaction, differing from one another in sign, magnitude, and dependence on interatomic distances. If, because of

thermal expansion, the lattice parameter reaches a certain critical value, at which a positive exchange integral changes sign, then there occurs a transition from the ferro- to an antiferromagnetic state.

No comparison has yet been made between experimental data for MnAs and these theories, because the elastic properties of this compound were not known. To improve our understanding of the nature of the magnetic transitions in manganese arsenide, we have measured the temperature dependence of Young's modulus E, of the shear modulus G, and of the coefficient of thermal expansion α in the temperature interval from room temperature to 460°K.

METHOD OF MEASUREMENT, RESULTS, AND DISCUSSION

1. The measurements of elastic properties were carried out by a resonance method, by means of a "composite rod" and excitation by piezoelectric quartz[7]. The measurements of Young's modulus were made with longitudinal oscillations, and of the shear modulus with torsional oscillations, at frequencies of order 60 kc/sec. Despite the high sensitivity of the measurement apparatus, which gives errors in the relative moduli of $\Delta E/E \sim 0.2\%$ and $\Delta G/G \sim 0.3\%$, the error in determination of the absolute values of the moduli, measured on different specimens of the same alloy, was no less than 8%, apparently because of different porosities of the specimens. Measurement of E and G on the same specimen permitted determination of Poisson's ratio $\mu = E/2G - 1$ and of the compressibility $\kappa = 3(1 - 2\mu)/E$.

The thermal expansion of MnAs was studied on specimens of length 50 mm and diameter 4 mm. Curves of the temperature dependence of the relative elongation were taken on a differential photoregistering Chévenard dilatometer, with magnification 466 along the temperature axis and 304 along the elongation axis. From the curves obtained values of the coefficient of thermal expansion $\alpha = \Delta l/l_0\Delta T$ were calculated by graphical differentiation.

2. Figure 1 shows the curves we obtained for the temperature dependence of the magnetization σ and of the inverse molar susceptibility $1/\chi_M$, measured at H = 10 kOe. In agreement with the data of other authors, an abrupt decrease of magnetization occurs at temperature 311°K, and there is a peak of the function $\chi_M(T)$ at temperature 392°K. The spontaneous magnetization of our specimens at temperature 77°K was $\sigma_S = 153$ G cm^3/g, which is somewhat larger than the values of σ_S obtained by other authors.

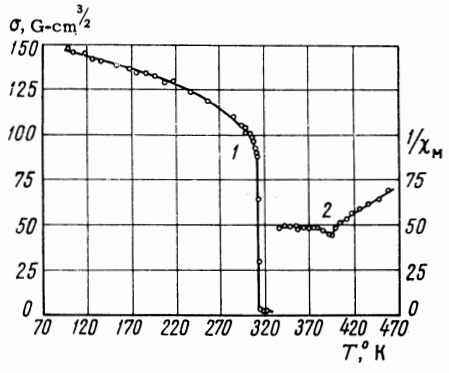

FIG. 1. Temperature dependence of magnetization (curve 1) and of the reciprocal of the molar susceptibility (curve 2), measured at H = 10 kOe.

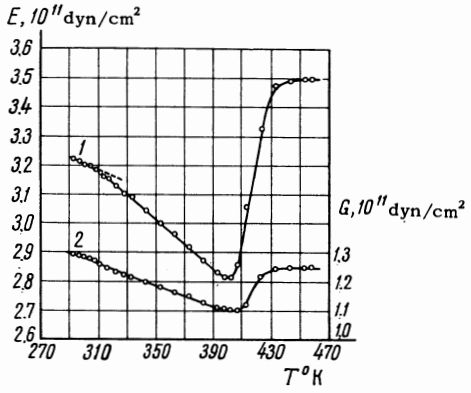

FIG. 2. Dependence of Young's modulus E (curve 1) and of the shear modulus (curve 2) on temperature.

Figure 2 shows the behavior of Young's modulus E and of the shear modulus G as functions of temperature. An anomalous rise of the moduli is observed in the neighborhood of temperature 400°K, that is in the vicinity of temperature Θ_2, where the peak is observed in the temperature dependence of the susceptibility. Here Young's modulus rises by 25%, the shear modulus by 13%. In the vicinity of temperature $\Theta_1 = 311$°K, where the abrupt decrease of magnetization occurs, no anomalous changes of the moduli were detected. The shear modulus diminishes linearly with rise of temperature, and the E(T) curve in the neighborhood of temperature Θ_1 undergoes only a slight change of slope. The values of the moduli at room temperature are

$$E = 3.22 \cdot 10^{11} \text{ dyn/cm}^2 \quad \text{and} \quad G = 1.29 \cdot 10^{11} \text{ dyn/cm}^2.$$

Figures 3 and 4 show the curves of temperature dependence of Poisson's ratio and of the compressibility of manganese arsenide. An abrupt change

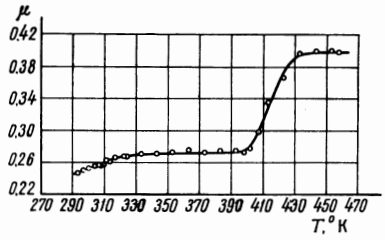

FIG. 3. Temperature dependence of Poisson's ratio.

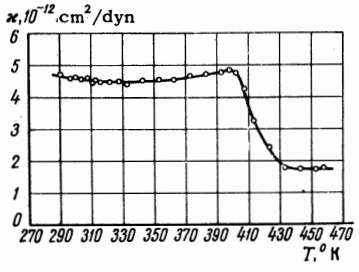

FIG. 4. Temperature dependence of compressibility.

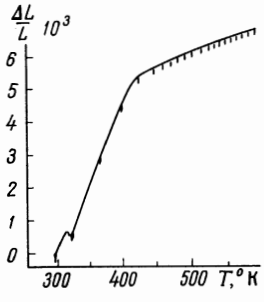

FIG. 5. Photo-record of dilatometer curve of the change of relative elongation of MnAs with temperature.

in the μ(T) and κ(T) curves is observed only in the neighborhood of temperature $\Theta_2 \sim 400$°K. Here Poisson's ratio increases from 0.27 to 0.40, and the compressibility falls from 4.5×10^{-12} to 1.7×10^{-12} cm^2/dyn. In the temperature interval from 290 to 400°K, the change of μ and κ with rise of temperature is very insignificant.

Figure 5 gives the photo-record of the dilatometer curve of change of relative elongation with temperature; Fig. 6 gives the temperature dependence of the coefficient of thermal expansion α, calculated from this curve. From these graphs it is clearly evident that the magnetic transition at temperature $\Theta_1 = 311$°K is accompanied by a discontinuous change of length of the specimen, whereas the transformation in the neighborhood of $\Theta_2 \sim 400$°K is accompanied by an abrupt change of α. The value of the volumetric coefficient of thermal expansion in the ferromagnetic range ($T < \Theta_1$) is $\alpha_V = 18 \times 10^{-5}$ deg^{-1}; in the paramagnetic range ($T > \Theta_2$), $\alpha_V = 6.9 \times 10^{-5}$ deg^{-1}.

These data agree qualitatively with results of an x-ray investigation of the temperature variation of

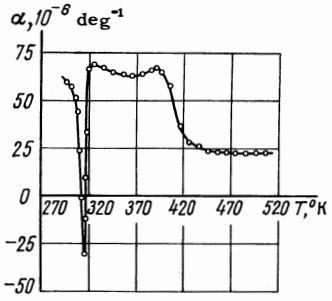

FIG. 6. Temperature dependence of coefficient of thermal expansion.

the crystal lattice parameters of MnAs, obtained by Willis and Rooksby[8]. Deviation from our data in quantitative respects affects chiefly the absolute value of the "jump" in length or in mean volume of the specimen in the transformation at the point Θ_1. The change of length of the specimen in the transformation at Θ_1 is considerably smaller according to the dilatometer measurements than from the x-ray data. Apparently this is connected with the fact that Willis and Rooksby did not take account of the change of symmetry connected with an orthorhombic distortion of the crystalline lattice of MnAs in the transformations Θ_1 and Θ_2, as established by Kornelsen[9] somewhat later.

3. We shall compare our data on the elastic properties with values of E and κ calculated according to the theories of[5] and[6].

Kittel[6] gives a formula for relating the value of Young's modulus to the shift of the transformation temperature with pressure, $d\Theta_1/dP$, and the thermal coefficient of linear expansion, α:

$$E = \frac{2}{\alpha(d\Theta_1/dP)}.$$

An estimate of E for manganese arsenide, by use of the experimental data $d\Theta_1/dP = -1.2 \times 10^{-8}$ deg dyn^{-1} cm^2, obtained by Rodbell, and the mean value of α determined from the x-ray data of Willis and Rooksby[8], gives for Young's modulus the value 4.2×10^{12} dyn cm^{-2}, which is an order of magnitude larger than our measured value $E = 3.22 \times 10^{11}$ dyn cm^{-2}.

Bean and Rodbell[5] regard the magnetic transformation in manganese arsenide at temperature $\Theta_1 = 313$°K as a transition from the ferromagnetic to the paramagnetic state. With the aid of the expressions obtained for the change of volume $\Delta v/v$ in the transformation and for a parameter η that determines the type of transition (for phase transitions of the first kind, $\eta > 1$),

$$\Delta v/v = N\varkappa kT_0\beta\sigma^2/2,\ \eta = 2.2Nk\varkappa T_0\beta^2,$$

a calculation was made of the compressibility κ of manganese arsenide and of the coefficient β that

determines the change of the magnetic transformation temperature as a function of volume. Here N is the number of atoms in unit volume, k is Boltzmann's constant, T_0 is the paramagnetic Curie point, and σ is the relative magnetization at the transformation temperature, referred to the magnetization at 77°K. By using the experimental data $\Delta v/v = 1.84 \times 10^{-2}$ [8], $T_0 = 285°K$ [2], $\sigma = 0.65$ [1], and $\eta = 2$, we calculated the coefficient β and the compressibility $\kappa = 2.2 \times 10^{-12}$ dyn^{-1} cm^2, which differs only by a factor 2 from our measured value $\kappa = 4.5 \times 10^{-12}$ dyn^{-1} cm^2.

4. Despite the fact that our experimental result coincides quite well with the value of κ calculated according to the theory of Bean and Rodbell, which denies the possibility of the existence of antiferromagnetic order in MnAs in the temperature interval from 313 to 400°K, the character of the change of elastic properties of manganese arsenide contradicts that statement. We mention two important features.

First, if the peak in the $\chi_M(T)$ curve is connected with structural changes of the crystal lattice, as is supposed in the theory of Bean and Rodbell [5], then it is cause for perplexity that the appearance of an orthorhombic distortion at 313°K produces no anomalies in the change of elastic properties, and yet that the disappearance of this distortion at 400°K leads to a large anomaly of Young's modulus and the shear modulus.

Second, the behavior of our E(T) and G(T) curves is very reminiscent of the behavior of antiferromagnets near the Néel temperature. As is known [10,11], upon transition of a material into an antiferromagnetic state a large diminution of the moduli E and G is observed; this is connected with a reorganization of the antiferromagnetic domain structure produced by external mechanical stresses. Simultaneous change of both moduli in the transformation is caused by the anisotropy of the exchange interactions in antiferromagnetic materials.

Our experimental results point to the presence in manganese arsenide of these peculiarities of the change of elastic properties, characteristic of an antiferromagnetic transformation. This gives us a basis for supposing that the magnetic transformation of MnAs at the point Θ_1 should be considered a transition from the ferromagnetic to an antiferromagnetic state, and that Θ_2 is the Néel temperature of this compound. The absence of quantitative agreement with the predictions of Kittel's theory may be connected with the approximate nature of the theoretical calculation.

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